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2-Nitrophenoxyacetanilide: a chain of rings generated by C—H$\cdots$O hydrogen bonds

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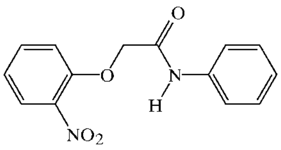
In molecules of the title compound, $C_{14}H_{12}N_2O_4$, the conformation is dominated by an intramolecular N—H$\cdots$O hydrogen bond in which one of the nitro O atoms is the acceptor. The molecules are linked by paired C—H$\cdots$O hydrogen bonds [H$\cdots$O = 2.41 Å, C$\cdots$O = 3.2990 (17) Å and C—H$\cdots$O = 156°] into centrosymmetric $R_2^2(14)$ dimers; these dimers are linked weakly into chains of alternating $R_2^2(14)$ and $R_4^4(40)$ rings by a second C—H$\cdots$O hydrogen bond [H$\cdots$O = 2.55 Å, C$\cdots$O = 3.5006 (15) Å and C—H$\cdots$O = 162°].

Comment

The title compound, (I) (Fig. 1), was designed to contain a wide variety of potential donors and acceptors of both hard and soft (Braga *et al.*, 1995; Desiraju & Steiner, 1999) hydrogen bonds. Thus, there are both N—H and C—H bonds to provide potential hydrogen-bond donors, and there are three types of O-atom sites as potential acceptors, namely the ether O, the carbonyl O and the nitro O atoms. In addition, the presence of two independent aryl groups offers the possibility of N—H$\cdots\pi$(arene) and C—H$\cdots\pi$(arene) hydrogen bonding, as well as aromatic π–π stacking interactions.



(I)

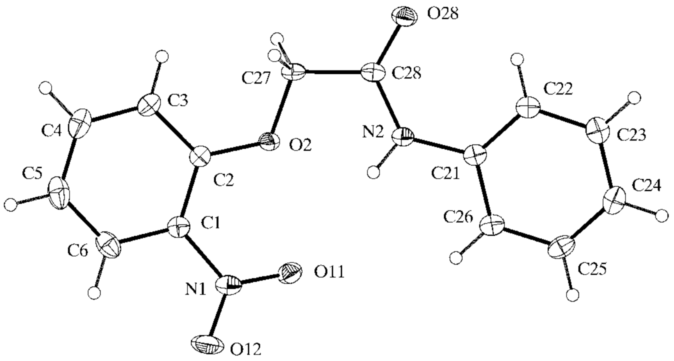


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

In the event, the only hard hydrogen bond is intramolecular, and this appears to be the dominant influence on the overall molecular conformation. Amine atom N2 acts as a donor to nitro atom O11 in a nearly linear N—H$\cdots$O hydrogen bond, so forming an *S*(9) motif (Bernstein *et al.*, 1995). In addition, there is a short contact to atom O2, but this contact is probably just an adventitious consequence of the hydrogen bond to atom O11. The consequences of the intramolecular hydrogen bonding are firstly the nearly planar overall conformation (Table 1), with a *cisoid* O2—C27—C28—N2 fragment, and secondly the unavailability of the NH group for participation in intermolecular hydrogen bonds. The bond angles in the central spacer unit are indicative of the strongly attractive nature of the intramolecular hydrogen bond. The dihedral angle between the nitro group and the adjacent aryl ring is 11.8 (2)°.

The supramolecular aggregation is determined by two C—H$\cdots$O hydrogen bonds, one weaker than the other (Table 2). In the stronger of these two interactions, aromatic atom C3 in the molecule at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O28 in the molecule at ($1-x, 1-y, 1-z$), so forming a centrosymmetric $S(9)[R_2^2(14)]S(9)$ (Bernstein *et al.*, 1995) dimer centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) (Fig. 2). These dimers are linked by the longer of the two intermolecular hydrogen bonds; atom C27 in the molecule at (x, y, z) acts as a donor *via* atom H27*A*

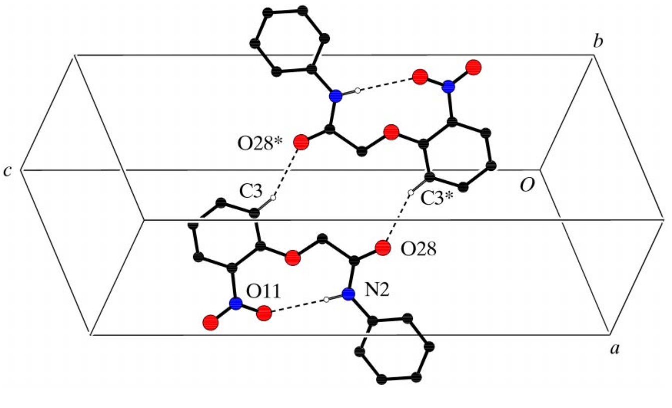


Figure 2
Part of the crystal structure of (I), showing the formation of a centrosymmetric hydrogen-bonded dimer. For clarity, the unit-cell box and H atoms bonded to C atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($1-x, 1-y, 1-z$).

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to nitro atom O11 in the molecule at (x, $1 + y$, z), so forming by translation a $C(7)$ chain parallel to [010]. Propagation of this hydrogen bond by translation and inversion then generates a complex chain of rings running parallel to the [010] direction, in which $R_2^2(14)$ rings centred at $(\frac{1}{2}, \frac{1}{2} + n, \frac{1}{2})$ (n = zero or integer) alternate with $R_4^4(40)$ rings centred at $(\frac{1}{2}, n, \frac{1}{2})$ (n = zero or integer) (Fig. 3).

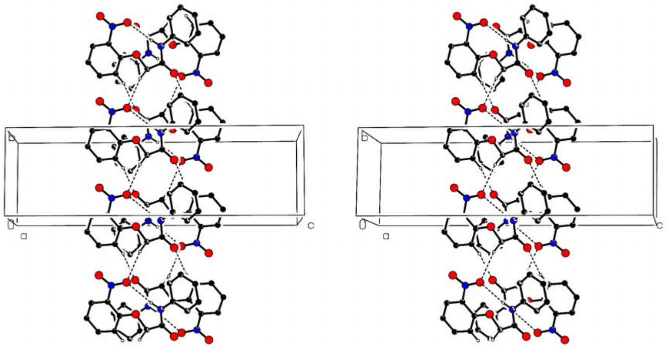

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a chain of alternating $R_2^2(14)$ and $R_4^4(40)$ rings along [010]. For clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted.

There are no direction-specific interactions between adjacent chains; in particular, there are no intermolecular hydrogen bonds involving the NH fragment, nor are there any C—H···π(arene) hydrogen bonds or aromatic π–π stacking interactions.

Experimental

For the preparation of (I), a suspension of $PhNH_2$ (10 mmol) in cold NaOH solution (20 ml of 1 mol dm^{-3}) was added to 2-nitrophenoxyacetyl chloride (10 mmol) (Minton & Stephen, 1922; Holley & Holley, 1952). The mixture was stirred for 1 h at 273 K and then allowed to reach ambient temperature. The precipitate that formed was collected after 16 h and recrystallized from ethanol, yielding the title compound [m.p. 394–395 K; literature m.p. 395–397 K (Kirk & Cohen, 1972)].

Crystal data

$C_{14}H_{12}N_2O_4$
$M_r = 272.26$
Monoclinic, $P2_1/n$
$a = 8.5855$ (3) Å
$b = 6.6129$ (2) Å
$c = 22.0221$ (8) Å
$\beta = 91.8330$ (17)°
$V = 1249.67$ (7) Å^3
$Z = 4$
$D_x = 1.447$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2869 reflections
$\theta = 3.2$–27.6°
$\mu = 0.11$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.40 × 0.30 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.951$, $T_{max} = 0.989$
5590 measured reflections
2869 independent reflections
2048 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 27.6°$
$h = -11 \rightarrow 11$
$k = -8 \rightarrow 8$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 1.05$
2869 reflections
182 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.0301P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.015 (2)

Table 1
Selected geometric parameters (°).

C2—O2—C27	118.86 (9)	C27—C28—N2	115.33 (11)
O2—C27—C28	108.62 (9)	C28—N2—C21	128.99 (11)
O2—C27—C28—N2	−8.14 (15)	C28—C27—O2—C2	167.20 (10)
C27—C28—N2—C21	−178.80 (12)	C1—C2—O2—C27	−168.01 (11)
C28—N2—C21—C22	9.4 (2)	C2—C1—N1—O11	−12.48 (18)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2	0.88	2.07	2.5517 (13)	113
N2—H2···O11	0.88	2.55	3.4191 (14)	172
C3—H3···O28^{i}	0.95	2.41	3.2990 (17)	156
C27—H27*A*···O11^{ii}	0.99	2.55	3.5006 (15)	162

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$.

Space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps and treated as riding atoms, with C—H distances of 0.95 (aromatic) and 0.99 Å (CH_2), and N—H distances of 0.88 Å, and with U_{iso}(H) values set at $1.2U_{eq}$(C,N).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1709). Services for accessing these data are described at the back of the journal.

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